VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

My name and post office address are as stated below:

That I am knowledgeable in the English and Japanese languages, and that I believe that the English translation of the Japanese application No. 2004-025833 filed on February 2, 2004 attached hereto is a true and complete translation of the above-identified Japanese application as filed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Name of the Material;	Claims	one(1)
	Specification	one(1)
	Abstract	one(1)

[Name of Document] Claims

[Claim 1]

A non-aqueous electrolytic solution for a lithium secondary battery comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous electrolytic solution contains a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60 and further contains a cyclohexybenzene compound having a benzene ring to which one or two halogen atoms are attached.

[Claim 2]

The non-aqueous electrolytic solution of claim 1, in which the cyclic carbonate compound comprises at least two compounds selected from ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate.

[Claim 3]

The non-aqueous electrolytic solution of claim 1, in which the linear carbonate compound comprises methyl ethyl carbonate.

[Claim 4]

A non-aqueous electrolytic solution for a lithium secondary battery comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous solution contains at least two cyclic carbonate compounds and a branched alkylbenzene compound in an amount of 0.01 wt.% to 3 wt.% and further a cyclohexybenzene compound having a benzene ring to which one or two halogen atoms are attached.

[Claim 5]

The non-aqueous electrolytic solution of claim 4, in which the cyclic carbonate compound comprises at least two compounds selected from ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate.

[Claim 6]

The non-aqueous electrolytic solution of claim 4, which further contains a linear carbonate compound.

[Claim 7]

The non-aqueous electrolytic solution of claim 6, in which the cyclic carbonate compound and linear carbonate compound are contained in a volume ratio of 20:80 to 40:60.

[Claim 8]

The non-aqueous electrolytic solution of claim 6, in which the linear carbonate compound comprises methyl ethyl carbonate.

[Claim 9]

The non-aqueous electrolytic solution of claim 4, in which the branched alkylbenzene compound is contained in a weight ratio of 0.1 to 1 based on the cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached.

[Claim 10]

The non-aqueous electrolytic solution of claim 4, in which the branched alkylbenzene compound is at least one compound selected from isopropylbenzene, cyclohexylbenzene, tert-butylbenzene, 1,3-di-tert-butylbenzene, tert-pentylbenzene, 4-tert-butylbiphenyl, tert-pentylbiphenyl, 4-tert-butyldiphenyl ether and 4-tert-pentyldiphenyl ether.

[Claim 11]

A lithium secondary battery comprising a positive electrode, a negative electrode and a non-aqueous electrolytic solution comprising an electrolyte dissolved in a non-aqueous solvent containing a cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached, in which the non-aqueous solvent comprises a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60.

[Claim 12]

The lithium secondary battery of claim 11, in which

the cyclic carbonate compound comprises at least two compounds selected from ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate.

[Claim 13]

The lithium secondary battery of claim 11, in which the linear carbonate compound comprises methyl ethyl carbonate.

[Claim 14]

A lithium secondary battery comprising a positive electrode, a negative electrode and a non-aqueous electrolytic solution comprising an electrolyte dissolved in a non-aqueous solvent containing a cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached, in which the non-aqueous solvent comprises at least two cyclic carbonate compounds and a branched alkylbenzene compound in an amount of 0.01 wt.% to 3 wt.%.

[Claim 15]

The lithium secondary battery of claim 14, in which the cyclic carbonate compound comprises at least two compounds selected from ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate.

[Claim 16]

The lithium secondary battery of claim 14, in which the branched alkylbenzene compound is contained in a weight ratio of 0.1 to 1 based on the cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached.

[Claim 17]

The lithium secondary battery of claim 14, in which the branched alkylbenzene compound is at least one compound selected from isopropylbenzene, cyclohexylbenzene, tert-butylbenzene, 1,3-di-tert-butylbenzene, tert-pentylbenzene, 4-tert-butylbiphenyl, tert-pentylbiphenyl, 4-

tert-butyldiphenyl ether and 4-tert-pentyldiphenyl ether.

[Name of Document] Specification

[Title of Invention] Non-aqueous electrolytic solution and lithium secondary battery using the same

[Field of Invention]

The present invention relates to a non-aqueous electrolytic solution employable for a lithium secondary battery showing improved battery performances such as safety in the case of overcharging and reduction of production of decomposition gases in the case of storage at high temperatures, and further relates to a lithium secondary battery employing the same.

[Background of Invention]

The lithium secondary battery which is recently employed widely for an electric source driving small-sized electronic tools/devices mainly comprises a positive electrode comprising a lithium complex oxide such as $LiCoO_2$ and a negative electrode comprising carbonaceous material or lithium metal. The lithium secondary battery employs a non-aqueous electrolytic solution comprising a carbonate compound such as ethylene carbonate (EC) or dimethyl carbonate (DMC).

[Disclosure of Invention]

[Problems solved by Invention]

It is recently requested that a battery give a high voltage and a high energy density. It is difficult, however to improve both the battery performances and safety. Particularly, a battery showing a high energy density is required to show high safety in the case of overcharging, compared with the conventional battery. However, it is difficult to maintain both of cycle characteristics and storage stability at high temperatures. Further, the battery tends to generate a gas resulting in expansion of the battery. In consideration of recent requirements for a secondary battery, the performances of the battery so

far developed do not satisfy the requirements. Therefore, the secondary battery should be further improved in safety while keeping the battery performances to satisfy future requirements for high energy density.

It has been known that addition of a small amount of an organic compound to an electrolytic solution can improve safety of a non-aqueous secondary battery in the case of overcharging.

JP2003-317803A discloses an invention for a non-aqueous secondary battery improved in its safety in the case of overcharging, which employs an electrolytic solution containing a cyclohexylbenzene having a benzene ring of which at least one hydrogen atom is replaced with a fluorine atom. However, there is a problem in the invention for improving safety in the case of overcharging which is disclosed in the above-mentioned patent publication. The problem resides in the fact that the invention is not satisfactorily applicable to a battery required to show both of a high voltage and a high energy density.

The invention has an object to provide a non-aqueous electrolytic solution which is favorably employable for manufacturing a lithium secondary battery that is free from the above-mentioned problems of a lithium secondary battery showing both of a high voltage and a high energy density, and hence to provide a non-aqueous electrolytic solution which is improved in safety in the case of overcharging, storage characteristics at high temperatures, reduction of expansion of a battery caused by generation of a gas.

[Means for solving the problems]

The invention relates to a non-aqueous electrolytic solution for a lithium secondary battery comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous electrolytic solution contains a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60 and further contains a

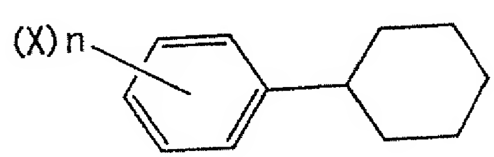
cyclohexybenzene compound having a benzene ring to which one or two halogen atoms are attached.

The invention further relates to a non-aqueous electrolytic solution for a lithium secondary battery comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous solution contains at least two cyclic carbonate compounds and a branched alkylbenzene compound in an amount of 0.01 wt.% to 3 wt.% and further a cyclohexybenzene compound having a benzene ring to which one or two halogen atoms are attached.

The invention further relates to a lithium secondary battery comprising a positive electrode, a negative electrode and a non-aqueous electrolytic solution comprising an electrolyte dissolved in a non-aqueous solvent containing a cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached, in which the non-aqueous solvent comprises a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60.

The invention furthermore relates to a lithium secondary battery comprising a positive electrode, a negative electrode and a non-aqueous electrolytic solution comprising an electrolyte dissolved in a non-aqueous solvent containing a cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached, in which the non-aqueous solvent comprises at least two cyclic carbonate compounds and a branched alkylbenzene compound in an amount of 0.01 wt.% to 3 wt.%.

In the invention, the cyclohexylbenzene compound having a benzene ring to which one or two halogen atoms are attached can be a compound having the following formula (I):



(I)

[in which X stands for a halogen atom and n is 1 or 2, provided that the position of the halogen atom is optional].

[Effects provided by Invention]

The present invention provides a lithium secondary battery which is improved in the safety in the case of overcharging, cycle characteristics, storage characteristics at high temperatures and reduction of expansion caused by generation of a gas.

[Preferred embodiment of Invention]

The electrolytic solution of the invention shows a lower viscosity as compared with the electrolytic solution disclosed in the aforementioned patent publication. Hence, the electrolytic solution of the invention can be easily incorporated in a battery, and further shows excellent resistance to overcharging and excellent cycle characteristics.

Since the electrolytic solution of the invention can be easily incorporated in a battery, a period required for incorporating an electrolytic solution into a battery can be shortened. The use of a specific amount of the branched alkylbenzene compound in combination of the cyclohexylbenzene compound having a benzene ring to which halogen atom(s) are attached according to the invention is effective to improve the safety in the case of overcharging.

Particularly, the non-aqueous electrolytic solution of the invention improves the safety in the case of overcharging as well as battery performance of a lithium secondary battery when the electrolytic solution containing the cyclohexylbenzene compound having a benzene ring to which halogen atom(s) are attached further contains a non-aqueous solvent comprising at least two cyclic carbonate compounds and 0.01 - 3 wt.% of a branched alkylbenzene compound.

According to the invention, a lithium secondary

batter is improved in the safety in the case of over-charging and cycle characteristics by the use of a non-aqueous electrolytic solution comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous electrolytic solution contains a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60 and further contains a cyclohexybenzene compound of the aforementioned formula (I) having a benzene ring to which halogen atom(s) are attached.

Examples of the cyclic carbonate compounds employable for the non-aqueous electrolytic solution preferably include ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate, and vinylethylene carbonate. More preferably, at least two cyclic carbonates selected from ethylene carbonate, propylene carbonate, vinylene carbonate and vinylethylene carbonate are employed. Most preferably, the non-aqueous electrolytic solution comprises ethylene carbonate and vinylene carbonate.

Examples of the linear carbonate compounds include linear carbonate compounds having an alkyl groups such as dimethyl carbonate (DMC), methyl ethyl carbonate (MEC), diethyl carbonate (DEC), methyl propyl carbonate (MPC), dipropyl carbonate (DPC), methyl butyl carbonate (MBC) and dibutyl carbonate (DBC). The alkyl group can be linear alkyl or branched alkyl.

The proportion of the cyclic carbonate compound and the linear carbonate compound comprised in the non-aqueous solvent preferably is in the range of 20:80 to 40:60 in terms of a volume ratio. If the electrolytic solution comprises the cyclic carbonate compound in excess of 40:60 in the volume ratio of the cyclic carbonate compound and the linear carbonate compound, the obtained solution tends to be too viscous to permeate into the battery. It is difficult to keep satisfactory cycle retention under influence of the high viscosity. The in-

fluence is remarkable in a battery of a high capacity or a high energy density such as a cylindrical battery or a square-shaped battery, particularly in a cylindrical or square-shaped battery having an electrode material layer of a high density in an electrode. If the electrolytic solution comprises the cyclic carbonate compound less than 20:80 in the volume ratio of the cyclic carbonate compound and the linear carbonate compound, the conductivity of the solution tends to be low and it is difficult to keep satisfactory cycle retention. Therefore, the volume ratio of the cyclic carbonate compound and the linear carbonate compound in the non-aqueous solvent preferably is in the range of 20:80 to 40:60, and more preferably in the range of 20:80 to 35:65.

The linear carbonate preferably has a methyl group to lower the viscosity. Accordingly, the linear carbonate preferably is dimethyl carbonate or methyl ethyl carbonate. Methyl ethyl carbonate, which has low viscosity, a melting point of -20°C or lower and a boiling point of 100°C or higher, is a particularly preferred asymmetrical linear carbonate. The asymmetrical linear carbonate, namely methyl ethyl carbonate can be used in combination with a symmetrical linear carbonate, namely dimethyl carbonate and/or diethyl carbonate in a volume ratio of 100:0 to 51:49 (particularly, 100:0 to 70:30).

In the present invention, the non-aqueous electrolytic solution, which contains a cyclohexylbenzene compound having a benzene ring to which halogen atom(s) are attached, preferably further contains at least two cyclic carbonate compounds and a branched alkylbenzene compound. The branched alkylbenzene compound can be contained in the solution in an amount of 0.01 wt.% to 3 wt.%. The interactions of the compounds can improve safety from overcharging, cyclic characteristics and high temperature storage characteristics. Further, gas generation is inhibited to prevent the battery from expanding. There-

fore, an excellent lithium secondary battery can be obtained according to the invention.

The non-aqueous electrolytic solution comprises an electrolyte in a non-aqueous solvent, which contains the compound represented by the formula (I). In the formula (I), X is a halogen atom, such as fluorine, chlorine, bromine and iodine, preferably is fluorine or chlorine, and most preferably is fluorine.

Examples of the compounds of the formula (I) having one X group include 1-fluoro-2-cyclohexylbenzene, 1-fluoro-3-cyclohexylbenzene, 1-fluoro-4-cyclohexylbenzene, 1-chloro-4-cyclohexylbenzene, 1-bromo-4-cyclohexylbenzene and 1-iodo-4-cyclohexylbenzene. Examples of the compounds having two X groups include 1,2-dichloro-3-cyclohexylbenzene, 1,3-dibromo-4-cyclohexylbenzene, 1,4-dichloro-2-cyclohexylbenzene, 1,2-difluoro-4-cyclohexylbenzene and 1,3-difluoro-5-cyclohexylbenzene. Particularly preferred are 1-fluoro-4-cyclohexylbenzene and 1,2-difluoro-4-cyclohexylbenzene. The compounds can be used singly or in combination.

An excessive amount of the compound of the formula (I) might lower battery performances. On the other hand, the amount of the compound is too small, satisfactory battery performances might not be given. Therefore, the amount preferably is 1 wt.% or more, more preferably is 1.5 wt.% or more, and most preferably is 2 wt.% or more, based on the weight of the non-aqueous electrolytic solution. Further, the amount preferably is 10 wt.% or less, more preferably is 7 wt.% or less, and most preferably is 5 wt.% or less.

The branched alkylbenzene compound, which is preferably used in combination with the cyclohexylbenzene compound of the formula (I), has a benzene ring such as benzene, biphenyl and diphenyl ether to which a branched alkyl group is attached. The most preferred compound has a benzene ring to which a branched alkyl group is at-

tached.

Examples of the branched alkylbenzene compounds include isopropylbenzene, cyclohexylbenzene, tert-butylbenzene, 1,3-di-tert-butylbenzene, tert-pentyl(amyl)-benzene, 4-tert-butylbiphenyl, tert-pentyl(amyl)biphenyl, bis(4-tert-butylphenyl) ether and bis(4-tert-pentyl-(amyl)phenyl) ether. Particularly preferred are cyclohexylbenzene, tert-butylbenzene and tert-pentyl(amyl)-benzene. One compound can singly be used, or two or more compounds can be used in combination.

An excessive amount of the branched alkylbenzene compound might lower battery performances. On the other hand, the amount of the compound is too small, satisfactory battery performances might not be provided. Therefore, the amount of the branched alkylbenzene compound preferably is 0.01 wt.% or more, more preferably is 0.1 wt.% or more, and most preferably is 0.5 wt.% or more, based on the weight of the non-aqueous electrolytic solution. Further, the amount preferably is 3 wt.% or less, more preferably is 2.5 wt.% or less, and most preferably is 2 wt.% or less. Addition of the branched alkylbenzene compound improves safety in the case of overcharging.

The weight ratio of the branched alkylbenzene compound to the compound of the formula (I) preferably is 0.1 or more, more preferably is 0.2 or more, and most preferably is 0.25 or more. Further, the weight ratio preferably is 1 or less, more preferably is 0.8 or less, and most preferably is 0.75 or less.

The cyclic carbonate compound contained in the non-aqueous electrolytic solution according to the invention preferably comprises at least two compounds selected from ethylene carbonate, propylene carbonate, butylene carbonate, vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate. The two compounds are more preferably selected from ethylene carbonate, propylene car-

bonate, vinylene carbonate and vinylethylene carbonate. It is particularly preferred to comprise ethylene carbonate and vinylene carbonate.

An excessive amount of the cyclic carbonate contained in the non-aqueous electrolytic solution might lower battery performances. On the other hand, the amount of the compound is too small, satisfactory battery performances might not be provided. Therefore, the amount of the cyclic carbonate compound contained in the non-aqueous electrolytic solution preferably is 20 vol.% or more, and more preferably is 25 vol.% or more. Further, the amount preferably is 40 vol.% or less, and more preferably is 35 vol.% or less.

The cyclic carbonate compound having an unsaturated carbon-carbon bond such as vinylene carbonate, dimethylvinylene carbonate and vinylethylene carbonate is contained in the non-aqueous solvent in an amount of preferably 0.1 vol.% or more, more preferably 0.4 vol.% or more, and most preferably 0.8 vol.% or more. Further, the compound is contained in an amount of preferably 8 vol.% or less, more preferably 4 vol.% or less and most preferably 3 vol.% or less.

Other non-aqueous solvents can also be used in the present invention. Examples of the other solvents include lactones such as γ-butyrolactone (GBL), γ-valerolactone, and α-angelica lactone; ethers such as tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1,2-dimethoxyethane, 1,2-diethoxyethane, and 1,2-dibutoxyethane; nitriles such as acetonitrile, and adiponitrile; linear esters such as methyl propionate, methyl pivalate, butyl pivalate, octyl pivalate, dimethyl oxalate, ethyl methyl oxalate, and diethyl oxalate; amides such as dimethylformamide; and compounds having the S=O bonding such as glycol sulfite, propylene sulfite, glycol sulfate, propylene sulfate, divinyl sulfone, 1,3-propane sultone, 1,4-butane sultone, and 1,4-butanediol dimethane

sulfonate.

The non-aqueous solvents can be used in combination. Examples of combinations of the non-aqueous solvents include a combination of cyclic carbonate and linear carbonate, a combination of cyclic carbonate and lactone, a combination of cyclic carbonate, lactone and linear ester, a combination of cyclic carbonate, linear carbonate and lactone, a combination of cyclic carbonate, linear carbonate and ether, and a combination of cyclic carbonate, linear carbonate and linear ester. Preferred are the combination of cyclic carbonate and linear carbonate, and the combination of cyclic carbonate, linear carbonate and linear ester.

The proportion of the cyclic carbonate compound and the linear carbonate compound comprised in the non-aqueous solvent preferably is in the range of 20:80 to 40:60 in terms of a volume ratio. If the electrolytic solution comprises the cyclic carbonate compound in excess of 40:60 in the volume ratio of the cyclic carbonate compound and the linear carbonate compound, the obtained solution tends to be too viscous to permeate into the battery. It is difficult to keep satisfactory cycle retention under influence of the high viscosity. The influence is remarkable in a battery of a high capacity or a high energy density such as a cylindrical battery or a square-shaped battery, particularly in a cylindrical or square-shaped battery having an electrode material layer of a high density in an electrode. If the electrolytic solution comprises the cyclic carbonate compound less than 20:80 in the volume ratio of the cyclic carbonate compound and the linear carbonate compound, the conductivity of the solution tends to be low and it is difficult to keep satisfactory cycle retention. Therefore, the volume ratio of the cyclic carbonate compound and the linear carbonate compound in the non-aqueous solvent preferably is in the range of 20:80 to 40:60, and more pre-

ferably in the range of 20:80 to 35:65.

The linear carbonate preferably has a methyl group to lower the viscosity. Accordingly, the linear carbonate preferably is dimethyl carbonate or methyl ethyl carbonate. Methyl ethyl carbonate, which has low viscosity, a melting point of -20°C or lower and a boiling point of 100°C or higher, is a particularly preferred asymmetrical linear carbonate. The asymmetrical linear carbonate, namely methyl ethyl carbonate can be used in combination with a symmetrical linear carbonate, namely dimethyl carbonate and/or diethyl carbonate in a volume ratio of 100:0 to 51:49 (particularly, 100:0 to 70:30).

An electrolyte is used in the non-aqueous electrolytic solution of the invention. Examples of the electrolytes include $LiPF_6$, $LiBF_4$ and $LiClO_4$. The examples further include lithium salts comprising a chain alkyl group such as $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, $LiC(SO_2CF_3)_3$, $LiPF_4(CF_3)_2$, $LiPF_3(C_2F_5)_3$, $LiPF_3(CF_3)_3$, $LiPF_3(iso\text{-}C_3F_7)_3$, and $LiPF_5(iso\text{-}C_3F_7)$, and lithium salts comprising a cyclic alkylene group such as $(CF_2)_2(SO_2)_2NLi$, and $(CF_2)_3(SO_2)_2NLi$. The electrolyte can be used singly or in combination. The concentration of the electrolyte salts in the non-aqueous solvent preferably is not less than 0.3 M, more preferably is not less than 0.5 M, and most preferably is not less than 0.7 M. Further, the concentration preferably is not more than 2.5 M, more preferably is not more than 1.5 M, and most preferably is not more than 1.2 M.

The electrolytic solution can be obtained according to the invention, for example, by preparing a non-aqueous solvent containing a cyclic carbonate compound and a linear carbonate compound, dissolving the electrolyte in the solvent, and further dissolving a compound of the formula (I), and if necessary the branched alkyl benzene compound in the solution.

The non-aqueous electrolytic solution of the invention has a kinetic viscosity at 25°C preferably in the

range of 2.3×10^{-6} to 3.6×10^{-6} m^2/s, more preferably in the range of 2.3×10^{-6} to 3.2×10^{-6} m^2/s, and most preferably in the range of 2.0×10^{-6} to 3.0×10^{-6} m^2/s. The kinetic viscosity can be measured by a capillary measurement using a Cannon-Fenske viscometer.

The non-aqueous electrolytic solution of the invention can contain air or carbon dioxide to reduce gas generation caused by decomposition of the electrolytic solution and to improve battery performances such as cycle and storage characteristics.

Carbon dioxide or air can be incorporated (dissolved) in the non-aqueous electrolytic solution in the invention according to a method (1) of bringing the non-aqueous electrolytic solution into contact with air or a carbon dioxide-containing gas to introduce the air or the gas into the solution, and then injecting the solution into a battery, or a method of (2) injecting the non-aqueous electrolytic solution into a battery, and then introducing air or a carbon dioxide-containing gas into a battery before or after sealing the battery. The two methods can be used in combination. The amount of the moisture contained in the air or carbon dioxide-containing gas preferably is as small as possible. The amount of water-vapor is so reduced that the due point of the air or gas preferably is lower than -40°C, and more preferably lower than -50°C.

The non-aqueous electrolytic solution of the invention is used for manufacturing a lithium secondary battery. There is no specific limitation with respect to materials of the lithium secondary battery other than the non-aqueous electrolytic solution of the present invention. The materials employed for the conventional lithium secondary battery can be used in the lithium secondary battery of the invention.

The positive electrode active material preferably is complex oxide of lithium with cobalt, manganese or nick-

el. The positive electrode active can be used singly or in combination. Examples of the complex lithium oxide include $LiCoO_2$, $LiMn_2O_4$, $LiNiO_2$ and $LiCo_{1-x}Ni_xO_2$ ($0.01<x<1$). The two or more positive electrode active materials can be mixed in an appropriate way. Examples of the mixtures include a mixture of $LiCoO_2$ with $LiMn_2O_4$, a mixture of $LiCoO_2$ with $LiNiO_2$, and a mixture of $LiMn_2O_4$ with $LiNiO_2$. The material more preferably is a complex lithium oxide showing voltage of 4.3 V or more such as $LiCoO_2$, $LiMn_2O_4$ and $LiNiO_2$ when the voltage of an open-circuit is measured using lithium as standard after completing the charge. The positive electrode active material most preferably is a complex metal oxide of lithium containing Co or Ni. A part of a complex metal oxide of lithium can be replaced with other metal. For example, a part of Co contained in $LiCoO_2$ can be replaced with Sn, Mg, Fe, Ti, Al, Zr, Cr, V, Ga, Zn or Cu.

A chemically inert electroconductive material can be used as a conductive material for the positive electrode. Examples of the conductive material include graphites such as natural graphite (e.g., scaly graphite), artificial graphite, and carbon blacks such as acetylene black, ketchen black, channel black, furnace black, lamp black, and thermal black. Graphite and carbon black can be used in combination at a certain mixing ratio. The positive electrode composite contains the conductive material preferably in an amount of 1 to 10 wt.%, and more preferably in an amount of 2 to 5 wt.%.

The positive electrode can be formed by mixing a positive electrode active material with a conductive material such as acetylene black or carbon black, and a binder to prepare a positive electrode composite material, coating a collecting sheet with the positive electrode material, and heating them at a temperature of about 50°C to 250_oC for about 2 hours under reduced pressure. Examples of the binders include polytetrafluoro-

ethylene (PTFE), polyvinylidene fluoride (PVDF), styrene /butadiene copolymer (SBR), acrylonitrile/butadiene copolymer (NBR), and carboxymethylcellulose (CMC). Examples of the collecting materials include aluminum foil and a stainless lath board.

A material capable of absorbing and releasing lithium can be used as a negative electrode (negative electrode active material). Examples of the material include: metallic lithium or lithium alloy; a carbonaceous material such as thermally decomposed carbon, coke, graphite (e.g., artificial graphite, natural graphite), a combustion product of an organic polymeric compound, or carbon fiber; tin or a tin compound; and silicon or a silicon compound. The carbonaceous material preferably has a distance (d_{002}) between lattice faces (002) of 0.340 nm or less. The carbonaceous material more preferably is graphite having a graphitic crystal structure with the distance (d_{002}) in the range of 0.335 to 0.340 nm. The negative electrode active can be used singly or in combination. A powdery material such as a powder of carbonaceous material can be used as a negative electrode composite material by mixing the material with a binder. Examples of the binders include ethylene/propylene diene terpolymer (EPDM), polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), styrene/butadiene copolymer (SBR), acrylonitrile/butadiene copolymer (NBR), and carboxymethyl-cellulose (CMC). There is no specific limitation with respect to the method for forming the negative electrode. The negative electrode can be prepared in the same manner as in the above-mentioned method for forming the positive electrode.

There is no specific limitation with respect to the structure of the lithium secondary battery. Examples of the structures are a coin-shaped battery, a cylindrical battery, and a square-shaped battery. The coin-shaped battery comprises a positive electrode, a negative elec-

trode, and a single-layered or a multi-layered separator. The cylindrical or square-shaped battery comprises a positive electrode, a negative electrode and a rolled separator. A known separator such as a microporous material of polyolefin, a fabric, and a non-woven fabric can be used. The separator for the battery can be a single layered porous film or a multi-layered porous film. The separator for the battery has gas permeability preferably in the range of 50 to 1,000 seconds per 100 cc, more preferably in the range of 100 to 800 seconds per 100 cc, and most preferably in the range of 300 to 500 seconds per 100 cc depending on the manufacturing conditions. In the case that the gas permeability is extremely high, the conductivity of lithium ion lowers to cause unsatisfactory function as battery separator. In the case that the gas permeability is extremely low, the mechanical strength lowers. The void volume ratio preferably is in the range of 30 to 60%, more preferably is in the range of 35 to 55%, and most preferably is in the range of 40 to 50%. The void ratio is so adjusted as to improve the battery capacity. The thickness of the separator for the battery is preferably thin to increase the energy density. Considering both of the mechanical strength and the performance increases if the thickness of the separator is small. The thickness of the separator preferably is in the range of 5 to 50 μm, more preferably in the range of 10 to 40μm, and most preferably in the range of 15 to 25 μm.

An effect of an additive provided in the invention depends on the density of an electrode material layer in a lithium secondary battery. The positive electrode composite layer formed on aluminum foil has a density of preferably in the range of 3.2 to 4.0 g/cm^3, more preferably in the range of 3.3 to 3.9 g/cm^3, and most preferably in the range of 3.4 to 3.8 g/cm^3. It is difficult to prepare a battery having a density of the positive electrode

of more than 4.0 g/cm^3. The negative electrode composite layer formed on copper foil has a density of preferably in the range of 1.3 to 2.0 g/cm^3, more preferably in the range of 1.4 to 1.9 g/cm^3, and most preferably in the range of 1.5 to 1.8 g/cm^3. It is difficult to prepare a battery having a density of the negative electrode of more than 2.0 g/cm^3.

In the invention, the positive electrode layer can have a thickness (per one side of the collector) in the range of 30 to 120 μm, and more preferably in the range of 50 to 100 μm. The negative electrode layer (per one side of the collector) has a thickness preferably in the range of 1 to 100 μm, and more preferably in the range of 3 to 70 μm. If the thickness the electrode layer in the lithium secondary battery of the invention is too small, the quantity of an active material in the electrode material layer is so low as to decrease the battery capacity. If the thickness of the electrode layer is too large, the cycle and rate characteristics unfavorably lower.

There is no specific limitation with respect to the structures of the lithium secondary battery. Examples of the structure include a coin-shaped battery, a cylindrical battery, a square-shaped battery, and a lamination battery. The battery comprises a positive electrode, a negative electrode, a porous separator and a non-aqueous electrolytic solution. The cylindrical or square-shaped battery is preferred.

The lithium secondary battery of the present invention shows excellent cycle characteristics for a long term even if the charging termination voltage is higher than 4.2 V. The battery can further show excellent cycle characteristics even if the charging termination voltage is 4.3 V or more. The discharging termination voltage can be 2.5 V or more, and further can be 2.8 V or more. There is no specific limitation with respect to the current level. The battery is generally discharged at a

constant current of 0.1 to 3 C. The lithium secondary battery of the present invention can be charged and discharged at a temperature of -40°C or higher, and preferably at 0°C or higher. Further, the battery can be charged and discharged at a temperature of 100°C or lower, and preferably 80°C or lower.

A safety valve can be attached to a sealing plate to keep the lithium secondary battery from increasing the inner pressure.

A part of the battery such as a battery cell (can) or a gasket can have a cut to comply with pressure increase. At least one of various conventional safety attachments (for example, overcurrent-preventing devices such as a fuse, a bimetal and a PTC device) is preferably attached to the battery.

Two or more lithium secondary batteries of the invention can be placed in a battery package in series and/or parallel. A safety circuit (which has functions of monitoring conditions such as voltage, temperature and current in each of the battery and/or in the combined batteries, and breaking the current) can be attached to the battery package in addition to a safety attachment such as a PTC element, a thermal fuse, a fuse, and/or a current breaker.

The battery of the present invention can be used in various devices such as a mobile phone, a notebook computer, PDA, a camcorder, a compact camera, a shaver, an electric machinery tool, and an automobile. The lithium secondary battery of the invention is highly reliable, and is advantageously used in devices requiring the charging current of 0.5 A or higher.

[Examples]

The present invention is described by referring to the following examples and comparison examples.

[Example 1]

(Preparation of non-aqueous electrolytic solution)

A non-aqueous solvent of EC:VC(vinylene carbonate):MEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 2 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene and 1 wt.% of cyclohexylbenzene were added to the non-aqueous electrolytic solution. The kinetic viscosity of the electrolytic solution was 2.7×10^{-6} m^2/s at 25°C.

(Preparation of lithium secondary battery and measurement of battery performance)

90 wt.% of $LiCoO_2$ (positive electrode active material), 5 wt.% of acetylene black (conductive material), and 5 wt.% of polyvinylidene fluoride (binder) were mixed. 1-methyl-2-pyrrolidone was added to the mixture to form slurry. A surface of aluminum foil was coated with the slurry. The mixture was dried, and molded under pressure to form a positive electrode. 95 wt.% of artificial graphite (negative electrode active material) having a graphitic crystalline structure with a distance (d_{002}) of 0.335 nm between lattice faces (002), and 5 wt.% of polyvinylidene fluoride (binder) were mixed. 1-methyl-2-pyrrolidone was added to the mixture to give a slurry.

A surface of copper foil was coated with the slurry. The mixture was dried, and molded under pressure to produce a negative electrode.

A battery was prepared using a separator comprising a microporous polypropylene film (thickness: 20 μm). The non-aqueous electrolytic solution was poured into the battery. Before sealing the battery, carbon dioxide having the dew point of -60°C was introduced into the battery to prepare a cylindrical battery having the 18650 size (diameter: 18 mm, height: 65 mm). A pressure release vent and an inner current breaker (PTC element) were attached

to the battery. The positive electrode had a density of 3.5 g/cm^3, and the negative electrode had a density of 1.6 g/cm^3. The positive electrode layer had a thickness of 70 μm (per one side of the collector), and the negative electrode layer had a thickness of 60 μm (per one side of the collector).

In a cycle test, the 18650 battery was charged with a constant current of 2.2 A (1C) at an elevated temperature (45°C) to reach 4.3 V. The battery was further charged under the constant voltage for 3 hours in total to reach the terminal voltage of 4.3 V. The battery was discharged under the constant current of 2.2 A (1C) to reach the terminal voltage of 3.0 V. The cycle of charge and discharge was repeated. The initial discharging capacity (mAh) was the essentially same as that of Comparison Example 1 (using 1 M $LiPF_6$+EC/VC/MEC (volume ratio) = 28:2:70 as the non-aqueous electrolytic solution to which 3 wt.% of cyclohexylbenzene was added in place of a specific cyclohexyl benzene compound such as 1-fluoro-4-cyclohexylbenzene). The battery performance was measured after 200 cycles, and the retention of the discharging capacity relative to the initial discharging capacity (100%) was 82.1%. Further, the amount of the generated gas after 200 cycles was remarkably smaller than that in the case of using no 1-fluoro-4-cyclohexylbenzene (Comparative Example 1).

After the cycle of charge and discharge was repeated five times, the 18650 battery was fully charged to reach 4.2 V at an ordinary temperature (20°C), and further charged with a constant current of 2.2A (1C) to conduct an overcharge test. The temperature on the surface of the battery was 120°C or lower, which is the standard highest temperature for safety. The conditions for preparation of the 18650 battery and the battery performance thereof are set forth in Table 1.

[Example 2]

A cylindrical battery was prepared in the same manner as in Example 1, except that 2 wt.% (based on the non-aqueous electrolytic solution) of 1,2-difluoro-4-cyclohexylbenzene was used in place of 1-fluoro-4-cyclohexylbenzene. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Example 3]

A cylindrical battery was prepared in the same manner as in Example 1, except that 1 wt.% (based on the non-aqueous electrolytic solution) of tert-pentylbenzene was used in place of cyclohexylbenzene. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Example 4]

A cylindrical battery was prepared in the same manner as in Example 1, except that 1 wt.% (based on the non-aqueous electrolytic solution) of tert-butylbenzene was used in place of cyclohexylbenzene. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging, the temperature on the surface of the battery was 120°C or lower.

[Example 5]

A cylindrical battery was prepared in the same manner as in Example 1, except that 1.5 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene, 1 wt.% of tert-pentylbenzene and 0.5 wt.% of cyclohexylbenzene were used. The obtained cylindrical

battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Example 6]

A non-aqueous solvent of EC:VC:MEC:PS (1,3-propanesultone) having a volume ratio of 28:2:69:1 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 2 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-3-cyclohexylbenzene and 1 wt.% of cyclohexylbenzene were added to the non-aqueous electrolytic solution.

A cylindrical battery was prepared in the same manner as in Example 1, except for the preparation of the solution. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Example 7]

A non-aqueous solvent of EC:VC:MEC:EMO(ethyl methyl oxalate) having a volume ratio of 28:2:69:1 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 2 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-2-cyclohexylbenzene and 1 wt.% of cyclohexylbenzene were added to the non-aqueous electrolytic solution.

A cylindrical battery was prepared in the same manner as in Example 1, except for the preparation of the solution. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Comparison Example 1]

A cylindrical battery was prepared in the same manner as in Example 1, except that a specific cyclohexylbenzene compound such as 1-fluoro-4-cyclohexylbenzene was not used, and 3 wt.% (based on the non-aqueous electrolytic solution) of cyclohexylbenzene was used. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Comparison Example 2]

A cylindrical battery was prepared in the same manner as in Example 1, except that a specific cyclohexylbenzene compound such as 1-fluoro-4-cyclohexylbenzene was not used, and 3 wt.% (based on the non-aqueous electrolytic solution) of tert-butylbenzene was used in place of cyclohexylbenzene. The obtained cylindrical battery showed a retention of discharging capacity after 200 cycles, as is set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was higher than 140°C. The effect of protection from overcharge was not observed in the same manner as in the case using no tert-butylbenzene.

[Comparison Example 3]

A non-aqueous solvent comprising EC:VC:DEC (volume ratio)=41:2:57 so as to comprise a cyclic carbonate and a linear carbonate in the weight ratio of 1:1 was prepared. To the non-aqueous solvent was added $LiPF_6$ to give a non-aqueous electrolytic solution containing 1M $LiPF_6$. To the non-aqueous electrolytic solution were added 1-fluoro-4-cyclohexylbenzene (1 wt.%) and cyclohexylbenzene (1 wt.%). A cylindrical battery was prepared in the same manner as in Example 1 except for employing the above-prepared non-aqueous electrolytic solution. Details and

a retention of discharging capacity after 200 cycles are set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

[Comparison Example 4]

A non-aqueous solvent comprising EC:VC:DEC (volume ratio)=13:2:85 was prepared. To the non-aqueous solvent was added $LiPF_6$ to give a non-aqueous electrolytic solution containing 1M $LiPF_6$. To the non-aqueous electrolytic solution were added 1-fluoro-4-cyclohexylbenzene (1 wt.%) and cyclohexylbenzene (1 wt.%). A cylindrical battery was prepared in the same manner as in Example 1 except for employing the above-prepared non-aqueous electrolytic solution. Details and a retention of discharging capacity after 200 cycles are set forth in Table 1. In the overcharging test, the temperature on the surface of the battery was 120°C or lower.

Table 1

	Electrolytic Solution (vol. ratio)	Cyclohexylbenzene compound (wt.%)	Branched benzene compound (wt.%)	Retention after 200 cycles (%)
Example 1	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-4-cyclohexylbenzene (2)	cyclohexylbenzene (1)	82.1
Example 2	1M $LiPF_6$ EC/VC/MEC =28/2/70	1,2-difluoro-4-cyclohexylbenzene (2)	cyclohexylbenzene (1)	82.4
Example 3	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-4-cyclohexylbenzene (2)	tert-pentylbenzene (1)	83.3

Example 4	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-4-cyclohexyl-benzene (2)	tert-butyl-benzene (1)	82.8
Example 5	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-4-cyclohexyl-benzene(1.5)	tert-pentyl-benzene (1) cyclohexyl-benzene (0.5)	83.2
Example 6	1M $LiPF_6$ EC/VC/MEC/PS =28/2/69/1	1-fluoro-3-cyclohexyl-benzene (2)	cyclohexyl-benzene (1)	84.1
Example 7	1M $LiPF_6$ EC/VC/MEC/EMO =28/2/69/1	1-fluoro-2 - cyclohexyl-benzene (2)	cyclohexyl-benzene (1)	82.5
Com. Ex. 1	1M $LiPF_6$ EC/VC/MEC =28/2/70	None	cyclohexyl-benzene (3)	74.6
Com. Ex. 2	1M $LiPF_6$ EC/VC/MEC =28/2/70	None	tert-butyl-benzene (3)	80.7
Com. Ex. 3	1M $LiPF_6$ EC/VC/MEC =41/2/57	1-fluoro-4-cyclohexyl-benzene (1)	cyclohexyl-benzene (1)	76.7
Com. Ex. 4	1M $LiPF_6$ EC/VC/MEC =13/2/85	1-fluoro-4-cyclohexyl-benzene (1)	cyclohexyl-benzene (1)	72.1

Remarks:

Positive electrode: $LiCoO_2$

Negative electrode: artificial graphite

Note: Overcharging preventive effect was observed in Examples 1-7 and Comparison Examples 1 and 3-4.

[Example 2-1]

(Preparation of non-aqueous electrolytic solution)

A non-aqueous solvent of EC:VC(vinylene carbonate):MEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene was added to the non-aqueous electrolytic solution. The dynamic viscosity of the electrolytic solution was 2.7×10^{-6} m^2/s at 25°C.

(Preparation of lithium secondary battery and measurement of battery performance)

90 wt.% of $LiCoO_2$ (positive electrode active material), 5 wt.% of acetylene black (conductive material), and 5 wt.% of polyvinylidene fluoride (binder) were mixed. 1-methyl-2-pyrrolidone was added to the mixture to give a slurry. A surface of aluminum foil was coated with the slurry. The coated foil was dried, and molded under pressure to form a positive electrode.

95 wt.% of artificial graphite (negative electrode active material) having a graphitic crystalline structure with a distance (d_{002}) of 0.335 nm between lattice faces (002), and 5 wt.% of polyvinylidene fluoride (binder) were mixed. 1-Methyl-2-pyrrolidone was added to the mixture to give a slurry. A surface of copper foil was coated with the slurry. The coated foil was dried, and molded under pressure to form a negative electrode.

A battery was prepared using a separator comprising a microporous polypropylene film (thickness: 20 μm). The non-aqueous electrolytic solution was poured into the battery. Before sealing the battery, carbon dioxide hav-

ing the dew point of -60°C was introduced into a battery can to prepare a cylindrical battery having the 18650 size (diameter: 18 mm, height: 65 mm). A pressure release vent and an inner current breaker (PTC element) were attached to the battery. The positive electrode had a density of 3.5 g/cm^3, and the negative electrode had a density of 1.6 g/cm^3. The positive electrode layer had a thickness of 70 μm (per one side of the collector), and the negative electrode layer had a thickness of 60 μm (per one side of the collector).

In a cycle test, the 18650 battery was charged with a constant current of 2.2 A (1C) at an elevated temperature (45°C) to reach 4.3 V. The battery was further charged under a constant voltage for 3 hours in total to reach the terminal voltage of 4.3 V. The battery was discharged under the constant current of 2.2 A (1C) to reach the terminal voltage of 3.0 V. The cycle of charge and discharge was repeated. The battery performance was measured after 200 cycles. The retention of discharging capacity relative to the initial discharging capacity (100%) was 81.3%. The battery performance is set forth in Table 2.

[Example 2-2]

A non-aqueous solvent of EC:VC:MEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-3-cyclohexylbenzene was added to the non-aqueous electrolytic solution in place of 1-fluoro-4-cyclohexylbenzene. The kinetic viscosity of the electrolytic solution was 2.7×10^{-6} m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 2-1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Example 2-3]

A non-aqueous solvent of EC:VC:MEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-2-cyclohexylbenzene was added to the non-aqueous electrolytic solution in place of 1-fluoro-4-cyclohexylbenzene. The kinetic viscosity of the electrolytic solution was 2.7×10^{-6} m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 2-1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Example 2-4]

A non-aqueous solvent of EC:VC:MEC:DMC having a volume ratio of 28:2:50:20 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene was added to the non-aqueous electrolytic solution. The kinetic viscosity of the electrolytic solution was 2.5×10^{-6} m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 2-1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Example 2-5]

A non-aqueous solvent of EC:VC:DEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene was added to the non-aqueous electrolytic solution. The dynamic viscosity of the electrolytic solution was 3.4×10^{-6} m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in

Example 2-1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Comparison Example 2-1]

A non-aqueous solvent of EC:VC:DEC having a volume ratio of 41:2:57 was prepared. The weight ratio of the cyclic carbonates to the linear carbonate was 1:1. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene was added to the non-aqueous electrolytic solution. The dynamic viscosity of the electrolytic solution was $3.7x10^{-6}$ m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Comparison Example 2-2]

A non-aqueous solvent of EC:VC:MEC having a volume ratio of 28:2:70 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of fluorobenzene was added to the non-aqueous electrolytic solution. The kinetic viscosity of the electrolytic solution was $2.7x10^{-6}$ m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 2-1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

[Comparison Example 2-3]

A non-aqueous solvent of EC:VC:DEC having a volume ratio of 13:2:85 was prepared. $LiPF_6$ was dissolved in the solvent to prepare 1 M non-aqueous electrolytic solution. 4 wt.% (based on the non-aqueous electrolytic solution) of 1-fluoro-4-cyclohexylbenzene was added to the non-

aqueous electrolytic solution. The dynamic viscosity of the electrolytic solution was 2.2×10^{-6} m^2/s at 25°C. A cylindrical battery was prepared in the same manner as in Example 1 using the electrolytic solution. The retention of discharging capacity after 200 cycles is set forth in Table 2.

Table 2

	Electrolytic Solution (vol. ratio)	Cyclohexyl-benzene compound (wt.%)	Retention after 200 cycles (%)
Example 2-1	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-4-cyclo-hexylbenzene (4)	81.3
Example 2-2	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-3-cyclo-hexylbenzene (4)	80.4
Example 2-3	1M $LiPF_6$ EC/VC/MEC =28/2/70	1-fluoro-2-cyclo-hexylbenzene (4)	80.7
Example 2-4	1M $LiPF_6$ EC/VC/MEC/DMC =28/2/50/20	1-fluoro-4-cyclo-hexylbenzene (4)	81.2
Example 2-5	1M $LiPF_6$ EC/VC/DEC =28/2/70	1-fluoro-4-cyclo-hexylbenzene (4)	79.7
Com. Ex. 2-1	1M $LiPF_6$ EC/VC/DEC =41/2/57	1-fluoro-4-cyclo-hexylbenzene (4)	76.9

Com. Ex. 2-2	1M $LiPF_6$ EC/VC/MEC =28/2/70	fluorobenzene (4)	78.6
Com. Ex. 2-3	1M $LiPF_6$ EC/VC/DEC =13/2/85	1-fluoro-4-cyclohexylbenzene (4)	70.2

Remarks:

Positive electrode: $LiCoO_2$

Negative electrode: artificial graphite

Comparison Example 2-2 employed 4 wt.% of fluorobenzene.

The present invention is not limited to the examples described above. The various combinations can be possible according to the invention. Particularly, the combinations of solvents cannot be limited to the working examples. Further, the present invention can be used for a square-shaped, coin-shaped or lamination battery, though the working examples were done for a cylindrical battery.

[Name of Document] Abstract
[Abstract]
[Object] To provide a lithium secondary battery showing improvement in safety in the case of overcharging, cycle characteristics, storage stability at high temperatures, and further in the prevention of expansion of battery caused by generation of gas.
[Invention] A non-aqueous electrolytic solution for a lithium secondary battery comprising an electrolyte dissolved in a non-aqueous solvent, wherein the non-aqueous electrolytic solution contains a cyclic carbonate compound and a linear carbonate compound in a volume ratio of 20:80 to 40:60 and further contains a cyclohexybenzene compound having a benzene ring to which halogen atom(s) are attached.